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(71) Applicant: **THE PROCTER & GAMBLE  
COMPANY**  
One Procter & Gamble Plaza  
Cincinnati Ohio 45202(US)

(72) Inventor: **Toen, Christiaan Arthur Jacques  
Kamiel**  
Boekweithofstraat 4  
B-2758 Haasdonk(BE)

(74) Representative: **Canonici, Jean-Jacques et al**  
Procter & Gamble European Technical  
Center N.V. Temselaan 100  
B-1820 Strombeek-Bever(BE)

(54) **Liquid detergent composition containing enzyme and enzyme stabilization system.**

(57) Stabilization systems for aqueous liquid detergent compositions containing detergent enzymes and perox-ygen bleaches are disclosed. The detergent compositions contain a carboxylic acid or a mixture of carboxylic acids as an enzyme stabilizing system.

**EP 0 378 261 A2**

**LIQUID DETERGENT COMPOSITION CONTAINING ENZYME AND ENZYME STABILIZATION SYSTEM**TECHNICAL FIELD

The present invention relates to a stabilization system for detergent enzymes. More particularly, it relates to a stabilization system for detergent enzymes in an aqueous liquid detergent composition which further contains a peroxygen bleach.

BACKGROUND OF THE INVENTION

EP 88-201009.3 discloses aqueous liquid detergent compositions containing a peroxygen bleach. The compositions are designed to limit the amount of available oxygen in solution. Enzyme-containing compositions are disclosed. The patent document does not disclose stabilization systems for the enzymes. At the time of filing of the present patent application, no publication of EP 88-201009.3 has taken place.

EP 28 865 discloses a stabilization system for enzymes in a liquid detergent composition comprising formic acid or a salt thereof and calcium ions. The disclosed compositions have a pH of from 6.5 to 8.5.

SUMMARY OF THE INVENTION

Unless otherwise specified, all percentages in the following are by weight.

The present invention relates to aqueous liquid detergent compositions comprising from 5 % to 60 % of an organic surfactant; from 1 % to 40 % of a peroxygen compound; a detergent enzyme; characterized in that it further comprises, as an enzyme stabilizing system, from 0.01 % to 15 % of a carboxylic acid of the formula X-R-COOH where X is H, OH or COOH and R is an unsubstituted or hydroxy substituted C<sub>1</sub> to C<sub>9</sub> alkyl, alkenyl, alkynyl or aryl group; and mixtures of said acids.

Preferred compositions have a pH of at least 8.5, more preferably at least 9.0, most preferably at least 9.5. The peroxygen compound preferably is a perborate, most preferably perborate tetrahydrate.

Preferred composition contain a water-miscible organic solvent such as ethanol. This reduces the solubility of any dispersed peroxygen compound, resulting in a low level of available oxygen in the liquid phase that is controlled to be under 0.5 %, preferably below 0.1 %.

The amount of carboxylic acid enzyme stabilizer preferably is from 0.5% to 10%, most preferably from 1% to 7.5%. Preferred enzyme stabilizers are acetic acid, propionic acid and adipic acid. Most preferred is adipic acid. According to the invention, mixture of these acids with formate is also suitable.

Suitable detergent enzymes include detergent proteases, detergent amylases, detergent lipases and detergent cellulases. Preferred detergent compositions herein are those that contain a detergent protease, preferably a high alkaline protease, from 0.01 % to 5 % on 8 KNPU/g basis, most preferably from 0.05 % to 2.5 %.

The detergent compositions optionally contain, as a second enzyme stabilizer, from 0.01 % to 5 % magnesium ions, preferably from 0.1 % to 0.5 %.

DETAILED DESCRIPTION OF THE INVENTION

In spite of their rapidly growing popularity, liquid detergent compositions available to date do not fully match the performance profile of high quality granular detergents, particularly of those containing a peroxygen bleach and detergent enzymes. It is, therefore, desirable to provide liquid detergent compositions that contain both a peroxygen bleach and detergent enzymes. Ways of doing so have been provided in our earlier patent application, EP 88-201009.3.

It has now been found that detergent enzymes present in aqueous, peroxygen bleach-containing liquid detergents are subject to two types of deactivation mechanisms. The first mechanism involves auto-hydrolysis of the enzyme, and could be referred to as autolysis. This type of deactivation is rather well

known in the detergent industry, and several enzyme stabilization systems have been proposed to reduce its effects. Autolysis becomes more of a problem as the pH of the liquid detergent composition increases. On the other hand, a high pH is conducive to a good performance of the peroxygen bleach.

The second mechanism of enzyme deactivation involves the oxidation of certain amino acids in the enzyme. This mechanism is specific to liquid detergents containing peroxygen bleach upon storage, and has heretofore not been recognized in the detergent industry.

An enzyme stabilization system for use in aqueous liquid detergent compositions which contain a peroxygen bleach should protect the enzyme against both autolysis and oxidative deactivation. Formic acid appears to protect against autolysis, but not against oxidative deactivation.

It has now surprisingly been found that certain carboxylic acids, to wit, acids of the formula  $X-R-COOH$ , where X is H, OH or COOH and R is an unsubstituted or hydroxy substituted  $C_1$  to  $C_9$  alkyl, alkenyl, alkynyl or aryl group protect enzymes against both oxidative deactivation and autolysis. Of course, these carboxylic acids become partially or totally deprotonated at the pH of the detergent composition, particularly when the pH of the composition is greater than 8.5, as is preferred for peroxygen bleach performance. Unless stated otherwise, the word "carboxylic acid" as used herein encompasses the deprotonated species and salts as well. The percentages herein are weight percentages, calculated on the basis of the protonated acid.

In practice, the acid or a water-soluble salt of the acid is added to the composition, and the composition's pH is adjusted to its desired value, using customary alkaline or acidic materials, as the case may be. As an alternative, the acid or its water soluble salt may be premixed with the enzyme hereinafter described, before being introduced into the composition. Said premix may also be evaporated or lyophilized so as to obtain solid particles which may be coated with, e.g. silicone oil. For the present purposes, the enzyme stabilizing compound will be referred to as the acid, even if it is present or added in the form of one of its salts.

It is understood that, according to the invention, mixtures of said acids can also be used.

It is also possible to premix the acid with the enzyme and then add the premix to the composition; in that case, lower acid concentrations can be obtained in the final compositions.

Preferred compositions contain carboxylic acids selected from acetic acid, propionic acid, adipic acid, and mixtures thereof.

The liquid detergent compositions herein all contain from 5 % to 60 % by weight of the liquid detergent composition, preferably from 15 % to 40 % of an organic surface-active agent selected from nonionic, anionic, cationic, and zwitterionic surface-active agents and mixtures thereof.

Synthetic anionic surfactants can be represented by the general formula  $R_1SO_3M$  wherein  $R_1$  represents a hydrocarbon group selected from the group consisting of straight or branched alkyl radicals containing from about 8 to about 24 carbon atoms and alkyl phenyl radicals containing from about 9 to about 15 carbon atoms in the alkyl group. M is a salt-forming cation which is typically selected from the group consisting of sodium, potassium, ammonium, and mixtures thereof.

A preferred synthetic anionic surfactant is a watersoluble salt of an alkylbenzene sulfonic acid containing from 9 to 15 carbon atoms in the alkyl group. Another preferred synthetic anionic surfactant is a water-soluble salt of an alkyl sulfate or an alkyl polyethoxylate ether sulfate wherein the alkyl group contains from about 8 to about 24, preferably from about 10 to about 18 carbon atoms and there are from about 1 to about 20, preferably from 1 to about 12 ethoxy groups. Other suitable anionic surfactants are disclosed in U.S. Patent 4,170,565, Flesher et al., issued October 9, 1979.

The nonionic surfactants are conventionally produced by condensing ethylene oxide with a hydrocarbon having a reactive hydrogen atom, e.g. a hydroxyl, carboxyl, or amino group, in the presence of an acidic or basic catalyst, and

include compounds having the general formula  $RA(CH_2CH_2O)_nH$  wherein R represents the hydrophobic moiety, A represents the group carrying the reactive hydrogen atom and n represents the average number of ethylene oxide moieties. R typically contains from about 8 to 22 carbon atoms. They can also be formed by the condensation of propylene oxide with a lower molecular weight compound. n usually varies from about 2 to about 24.

The hydrophobic moiety of the nonionic compound is preferably a primary or secondary, straight or branched, aliphatic alcohol having from about 8 to 24, preferably from about 12 to about 20 carbon atoms. A more complete disclosure of suitable nonionic surfactants can be found in U.S. Patent 4,111,855. Mixtures of nonionic surfactants can be desirable.

Suitable cationic surfactants include quaternary ammonium compounds of the formula  $R_1R_2R_3R_4N^+$  where  $R_1$ ,  $R_2$ , and  $R_3$  are methyl groups and  $R_4$  is a  $C_{12}$ - $C_{15}$  alkyl group, or where  $R_1$  is an ethyl or hydroxy ethyl group,  $R_2$  and  $R_3$  are methyl groups and  $R_4$  is a  $C_{12}$ - $C_{15}$  alkyl group.

Zwitterionic surfactants include derivatives of aliphatic quaternary ammonium, phosphonium, and

5 sulphonium compounds in which the aliphatic moiety can be a straight or branched chain and wherein one of the aliphatic substituents contains from about 8 to about 24 carbon atoms and another substituent contains, at least, an anionic water-solubilizing group. Particularly preferred zwitterionic materials are the ethoxylated ammoniumsulfonates and sulfates disclosed in U.S. Patents 3,925,262, Laughlin et al., issued December 9, 1975 and 3,929,678, Laughlin et al., issued December 30, 1975.

Semi-polar nonionic surfactants include water-soluble amine oxides containing one alkyl or hydroxy alkyl moiety of from about 8 to about 28 carbon atoms and two moieties selected from the group consisting of alkyl groups and hydroxy alkyl groups, containing from 1 to about 3 carbon atoms which can optionally be joined into ring structures.

10 Suitable anionic synthetic surface-active salts are selected from the group of sulfonates and sulfates. The like anionic detergents are well-known in the detergent arts and have found wide-spread application in commercial detergents. Preferred anionic synthetic water-soluble sulfonate or sulfate salts have in their molecular structure an alkyl radical containing from about 8 to about 22 carbon atoms.

15 Examples of such preferred anionic surfactant salts are the reaction products obtained by sulfating C<sub>8</sub>-C<sub>18</sub> fatty alcohols derived from tallow and coconut oil; alkylbenzene sulfonates wherein the alkyl group contains from about 9 to 15 carbon atoms; sodium alkylglyceryl ether sulfonates; ether sulfates of fatty alcohols derived from tallow and coconut oils; coconut fatty acid monoglyceride sulfates and sulfonates; and water-soluble salts of paraffin sulfonates having from about 8 to about 22 carbon atoms in the alkyl chain. Sulfonated olefin surfactants as more fully described in e.g. U.S. Patent Specification 3,332,880 can also be used. The neutralizing cation for the anionic synthetic sulfonates and/or sulfates is represented by conventional cations which are widely used in detergent technology such as sodium and potassium.

A particularly preferred anionic synthetic surfactant component herein is represented by the water-soluble salts of an alkylbenzene sulfonic acid, preferably sodium alkylbenzene sulfonates having from about 10 to 13 carbon atoms in the alkyl group.

25 A preferred class of nonionic ethoxylates is represented by the condensation product of a fatty alcohol having from 12 to 15 carbon atoms and from about 2 to 10, preferably 3 to 7 moles of ethylene oxide per mole of fatty alcohol. Suitable species of this class of ethoxylates include: the condensation product of C<sub>12</sub>-C<sub>15</sub> oxo-alcohols and 7 moles of ethylene oxide per mole of alcohol; the condensation product of narrow cut C<sub>14</sub>-C<sub>15</sub> oxo-alcohols and 7 or 9 moles of ethylene oxide per mole of fatty(oxo)alcohol; the condensation product of a narrow cut C<sub>12</sub>-C<sub>13</sub> fatty(oxo)alcohol and 6.5 moles of ethylene oxide per mole of fatty alcohol; and the condensation products of a C<sub>10</sub>-C<sub>14</sub> coconut fatty alcohol with a degree of ethoxylation (moles EO/mole fatty alcohol) in the range from 5 to 8. The fatty oxo alcohols while mainly linear can have, depending upon the processing conditions and raw material olefins, a certain degree of branching, particularly short chain such as methyl branching.

35 A degree of branching in the range from 15 % to 50 % (weight%) is frequently found in commercial oxo alcohols.

Preferred nonionic ethoxylated components can also be represented by a mixture of 2 separately ethoxylated nonionic surfactants having a different degree of ethoxylation. For example, the nonionic ethoxylate surfactant containing from 3 to 7 moles of ethylene oxide per mole of hydrophobic moiety and a second ethoxylated species having from 8 to 14 moles of ethylene oxide per mole of hydrophobic moiety. A preferred nonionic ethoxylated mixture contains a lower ethoxylate which is the condensation product of a C<sub>12</sub>-C<sub>15</sub> oxo-alcohol, with up to 50 % (wt) branching, and from about 3 to 7 moles of ethylene oxide per mole of fatty oxo-alcohol, and a higher ethoxylate which is the condensation product of a C<sub>16</sub>-C<sub>19</sub> oxo-alcohol with more than 50 % (wt) branching and from about 8 to 14 moles of ethylene oxide per mole of branched oxo-alcohol.

45 Suitable bleaches in the present compositions are solid, water-soluble peroxygen compounds. Preferred compounds include perborates, persulfates, peroxydisulfates, perphosphates and the crystalline peroxyhydrates formed by reacting hydrogen peroxyde with sodium carbonate or urea. Preferred peroxygen bleach compounds are sodium perborate monohydrate and sodium perborate tetrahydrate and sodium percarbonate. Perborate bleaches in the present composition can be in the form of small particles i.e. from 0.1 to 20 micrometers, said particles having been formed by in situ crystallization of the perborate.

50 The term "in situ crystallization" relates to processes whereby perborate particles are formed from larger particles or from solution, in the presence of the water/anionic surfactant/detergent builder matrix. This term therefore encompasses processes involving chemical reactions, as when sodium perborate is formed by reacting stoichiometric amounts of hydrogen peroxide and sodium metaborate or borax. It also encompasses processes involving dissolution and recrystallization, as in the dissolution of perborate monohydrate and subsequent formation of perborate tetrahydrate. Recrystallization may also take place by allowing perborate monohydrate to take up crystal water, whereby the monohydrate directly recrystallizes

into the tetrahydrate, without dissolution step.

In one embodiment of the invention, a perborate compound, e.g., sodium perborate monohydrate, is added to an aqueous liquid comprising the anionic surfactant and the detergent builder. The resulting slurry is stirred. During this stirring the perborate compound undergoes a process of dissolution/recrystallization. Due to the presence of the anionic surfactant and the detergent builder this dissolution/recrystallization process results in particles having the desired particle diameter.

As the monohydrate is more susceptible to recrystallization, the monohydrate is preferred for this embodiment of the invention. Particle diameters herein are weight average particle diameters, unless otherwise specified. For reasons of physical stability it is preferred that the particle size distribution is relatively narrow; i.e., it is preferred that less than 10 % (wt) has a particle diameter greater than 10 micrometers.

In a second embodiment of the invention the perborate compound is formed in situ by chemical reaction. For example, sodium metaborate is added to an aqueous liquid comprising the anionic surfactant and the detergent builder. Then a stoichiometric amount of hydrogen peroxide is added while stirring. Stirring is continued until the reaction is complete.

Instead of metaborate, other borate compounds, including e.g., borax and boric acid can be used. If borax is used as the boron compound, a stoichiometric amount of a base, e.g. sodium hydroxide, is added to ensure reaction of the borax to metaborate. The process then proceeds as described hereinabove for metaborate conversion. Instead of hydrogen peroxide, other peroxides may be used (e.g., sodium peroxide), as known in the art.

Preferred liquid detergent compositions contain, in addition to water, a water-miscible organic solvent. The solvent reduces the solubility of perborate in the liquid phase and thereby enhances the chemical stability of the composition.

It is not necessary that the organic solvent be fully miscible with water, provided that enough of the solvent mixes with the water of the composition to affect the solubility of the perborate compound in the liquid phase.

The water-miscible organic solvent must, of course be compatible with the perborate compound at the pH that is used. Therefore, polyalcohols having vicinal hydroxy groups (e.g. 1,2-propanediol and glycerol) are less desirable.

Examples of suitable water-miscible organic solvents include the lower aliphatic monoalcohols, and ethers of diethylene glycol and lower monoaliphatic monoalcohols. Preferred solvents are ethanol, isopropanol, 1-methoxy, 2-propanol, butyldiglycolether and ethyldiglycolether.

The compositions according to the invention also contain detergent enzymes; suitable enzymes include the detergent proteases, amylases, lipases, cellulases and mixtures thereof. Preferred enzymes are high alkaline proteases e.g. Maxacal (R) and Savinase (R).

Silicone-coated enzymes, as described in EP-A-0238216 can also be used.

Preferred compositions herein optionally contain as a builder a fatty acid component. Preferably, however, the amount of fatty acid is less than 5 % by weight of the composition, more preferably less than 4 %. Preferred saturated fatty acids have from 10 to 16, more preferably 12 to 14 carbon atoms. Preferred unsaturated fatty acids are oleic acid and palmitoleic acid.

Preferred compositions contain an inorganic or organic builder. Examples of inorganic builders include the phosphorous-based builders, e.g., sodium tripolyphosphate, sodium pyrophosphate, and aluminosilicates (zeolites).

Examples of organic builders are represented by polyacids such as citric acid, nitrilotriacetic acid, and mixtures of tartrate monosuccinate with tartrate disuccinate. Preferred builders for use herein are citric acid and alk(en)yl-substituted succinic acid compounds, wherein alk(en)yl contains from 10 to 16 carbon atoms. An example of this group of compounds is dodeceny succinic acid. Polymeric carboxylate builders inclusive of polyacrylates, polyhydroxy acrylates and polyacrylates/polymaleates copolymers can also be used.

The compositions herein can contain a series of further optional ingredients which are mostly used in additive levels, usually below about 5 %. Examples of the like additives include : suds regulants, opacifiers, agents to improve the machine compatibility in relation to enamel-coated surfaces, bactericides, dyes, perfumes, brighteners and the like.

The liquid compositions herein can contain further additives of a level from 0.05 % to 5 %. These additives include polyaminocarboxylates such as ethylenediaminetetracetic acid, diethylenetriaminopentacetic acid, ethylenediamino disuccinic acid or the water-soluble alkali metals thereof. Other additives include organo-phosphonic acids; particularly preferred are ethylenediamino tetramethylenephosphonic acid, hexamethylenediamino tetramethylenephosphonic acid, diethylenetriamino

pentamethylenephosphonic acid and aminotrimethylenephosphonic acid.

Bleach stabilizers such as ascorbic acid, dipicolinic acid, sodium stannates and 8-hydroxyquinoline can also be included in these compositions, at levels from 0.01 % to 1 %.

5 The beneficial utilization of the claimed compositions under various usage conditions can require the utilization of a suds regulant. While generally all detergent suds regulants can be utilized preferred for use herein are alkylated polysiloxanes such as dimethylpolysiloxane also frequently termed silicones. The silicones are frequently used in a level not exceeding 1.5 %, most preferably from 0.1 % to 1.0 %.

10 It can also be desirable to utilize opacifiers in as much as they contribute to create a uniform appearance of the concentrated liquid detergent compositions. Examples of suitable opacifiers include : polystyrene commercially known as LYTRON 621 manufactured by MONSANTO CHEMICAL CORPORATION. The opacifiers are frequently used in an amount from 0.3 % to 1.5 %.

The liquid detergent compositions of this invention can further comprise an agent to improve the washing machine compatibility, particularly in relation to enamel-coated surfaces.

15 It can further be desirable to add from 0.1 % to 5 % of known antiredeposition and/or compatibilizing agents. Examples of the like additives include : sodium carboxymethylcellulose; hydroxy-C<sub>1-6</sub>-alkylcellulose; polycarboxylic homo- or copolymeric ingredients, such as : polymaleic acid; a copolymer of maleic anhydride and methylvinylether in a molar ratio of 2:1 to 1:2; and a copolymer of an ethylenically unsaturated monocarboxylic acid monomer, having not more than 5, preferably 3 or 4 carbon atoms, for example (meth)-acrylic acid, and an ethylenically unsaturated dicarboxylic acid monomer having not more  
20 than 6, preferably 4 carbon atoms, whereby the molar ratio of the monomers is in the range from 1:4 to 4:1, said copolymer being described in more detail in European Patent Application 0 066 915, filed May 17, 1982.

The following examples illustrate the invention and facilitate its understanding.

25 Liquid detergent compositions were prepared by mixing the listed ingredients in the stated proportions. The pH of these compositions is in the range of from 9.5 to 10.5.

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	INGREDIENTS	COMPOSITION (by weight %)							
		I	II	III	IV	V	VI	VII	VIII
5	Water	28.5	28.5	30.0	29.0	30.5	26.0	27.5	25.5
	Ethanol	13.0	10.0	11.0	12.0	8.0	13.0	10.0	10.0
	Linear dodecylbenzene sulfonic acid	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
	Sodium cocoyl sulfate	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Condensation product of 1 mole of C <sub>13</sub> -C <sub>15</sub> oxoalcohol and 7 moles of ethylene oxide	7.0	7.0		7.0	7.0		7.0	
10	Condensation product of 1 mole of C <sub>13</sub> -C <sub>15</sub> oxoalcohol and 5 moles of ethylene oxide			7.0			7.0		7.0
	C <sub>12</sub> -C <sub>14</sub> (2hydroxyethyl) dimethyl ammonium chloride			0.5					1.0
15	Dodecenyl succinic acid	12.5			12.5			12.5	
	Dodecenyl-tetradecenyl succinic acid								
	Coconut fatty acid		15.0				15.0		
	TMS/TDS <sup>™</sup>			12.5					
20	Sodium tripolyphosphate					15.0			
	Zeolite								15.0
	Citric acid	0.8	0.8	0.8	1.0	1.0	0.8	3.0	0.8
	Oleic acid	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Diethylene triamine pentamethylene phosphonic acid	0.7	0.7		0.7	0.7		0.7	0.7
25	Hexamethylene diaminetetra (methylene phosphonic acid)			0.7			0.7		
	Sodium perborate monohydrate	14.5	14.5	14.5	14.5	14.5	14.5	14.5	14.5
	Protease 8KNPU/g	0.6	0.6		0.6		0.6	0.6	
30	Protease 16KNPU/g			0.3		0.3			0.3
	Protease mixture <sup>*</sup>								
	Amylase	0.2		0.2	0.2	0.2		0.2	0.2
	Sodium formate	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Sodium acetate						2.5		2.5
35	Sodium propionate				2.5				
	Adipic acid	2.5						2.5	2.5
	Succinic acid					2.5			
	Suberic acid		2.5						
	Maleic acid			2.5					
40	Magnesium acetate tetrahydrate							1.5	
	Sodium hydroxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
	Perfume and minors	balance							

<sup>\*</sup> aqueous protease solution containing by weight 20% protease 8KNPU/g, 5% adipic acid sodium hydroxide to balance the pH to 9.5

<sup>™</sup> (80:20) mixture of tartrate monosuccinate/tartrate disuccinate

INGREDIENTS	COMPOSITION (by weight %)							
	IX	X	XI	XII	XIII	XIV	XV	XVI
Water	31.0	37.0	24.5	32.5	31.0	35.5	31.5	34.5
Ethanol	8.0	8.0	13.0	8.0	13.0	8.0	10.0	8.0
Linear dodecylbenzene sulfonic acid	9.0	9.0	9.0	9.0	9.0	9.0	9.0	9.0
Sodium cocoyl sulfate								
Condensation product of 1 mole of C <sub>13</sub> -C <sub>15</sub> oxoalcohol and 7 moles of ethylene oxide			7.0			7.0		
Condensation product of 1 mole of C <sub>13</sub> -C <sub>15</sub> oxoalcohol and 5 moles of ethylene oxide	7.0	7.0		7.0	7.0		7.0	7.0
C <sub>12</sub> -C <sub>14</sub> (2hydroxyethyl) dimethyl ammonium chloride	0.5	0.5	0.5	1.0	0.5	0.5	1.0	0.5
Dodecanyl succinic acid								
Dodecanyl-tetradecanyl succinic acid		10.0			10.0		10.0	10.0
Coconut fatty acid			15.0					
TMS/TDS <sup>*</sup>				12.5		12.5		
Sodium tripolyphosphate							15.0	
Zeolite	15.0							
Citric acid	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Oleic acid								
Diethylene triamine pentamethylene phosphonic acid		0.7						
Hexamethylene diaminetetra (methylene phosphonic acid)	0.7			0.7	0.7			0.7
Sodium perborate monohydrate	14.5	14.5	14.5	14.5	14.5	14.5	14.5	14.5
Protease 8KNPU/g				0.6		0.6		
Protease 16KNPU/g	0.3	0.3	0.3		0.3		0.3	
Protease mixture <sup>*</sup>								3.0
Amylase			0.2	0.2			0.2	
Sodium formate	1.0	1.5	1.5			1.0		1.5
Sodium acetate	2.5	2.5	2.5	5.0	2.5	2.5	2.5	
Sodium propionate								
Adipic acid			2.5		2.5			
Succinic acid								
Suberic acid								
Maleic acid								
Magnesium acetate tetrahydrate	1.7							
Sodium hydroxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Perfume and minors	balance							

<sup>\*</sup> aqueous protease solution containing by weight 20% protease 8KNPU/g, 5% adipic acid sodium hydroxide to balance the pH to 9.5

<sup>\*\*</sup> (80:20) mixture of tartrate monosuccinate/tartrate disuccinate

## Claims

1. An aqueous liquid detergent composition comprising organic surfactants; a peroxygen bleach compound; a detergent enzyme; characterized in that it further comprises, as an enzyme stabilizing system, from 0.01% to 15% of a carboxylic acid of the formula X-R-COOH, where X is H, OH or COOH and R is an unsubstituted or hydroxy substituted C<sub>1</sub> to C<sub>9</sub> alkyl, alkenyl, alkynyl or aryl group; and mixtures of said acids.
2. An aqueous liquid detergent composition according to Claim 1, having a pH of at least 8.5, preferably



at least 9.0, most preferably at least 9.5.

3. An aqueous liquid detergent composition according to Claim 1 or 2 wherein the peroxygen compound is a perborate.

4. An aqueous liquid detergent composition according to Claim 1 or 2 wherein the peroxygen  
5 compound is a percarbonate.

5. An aqueous liquid detergent composition according to Claim 3, comprising a water-miscible organic solvent such that the perborate compound is present as a dispersion of solid particles and the amount of available oxygen in solution is less than 0.5 %, preferably less than 0.1 %.

6. An aqueous liquid detergent composition according to any one of the preceding claims, wherein the  
10 amount of the carboxylic acid enzyme stabilizer is from 0.01 % to 10 %, preferably from 0.1 % to 7.5 %.

7. An aqueous liquid detergent composition according to any one of the preceding claims wherein the carboxylic acid enzyme stabilizer is selected from acetic acid, propionic acid, adipic acid, and mixtures thereof, and mixtures of these carboxylic acids with formate.

8. An aqueous liquid detergent composition according to anyone of the preceding claims wherein the  
15 detergent enzyme is selected from the group consisting of detergent proteases, detergent amylases, detergent lipases, detergent cellulases, and mixtures thereof.

9. An aqueous liquid detergent composition according to Claim 8 wherein the detergent enzyme comprises detergent protease, preferably high alkaline protease.

10. An aqueous detergent composition according to any one of Claims 2-9, comprising, as a second  
20 enzyme stabilizer, from 0.01 % to 5 % magnesium ions.

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(71) Applicant: **THE PROCTER & GAMBLE  
COMPANY**  
One Procter & Gamble Plaza  
Cincinnati Ohio 45202(US)

(72) Inventor: **Tooen, Christiaan Arthur Jacques  
Kamiel**  
Boekweithofstraat 4  
B-2758 Haasdonk(BE)

(74) Representative: **Canonici, Jean-Jacques et al**  
Procter & Gamble European Technical  
Center N.V. Temselaan 100  
B-1853 Strombeek-Bever(BE)

(54) **Liquid detergent composition containing enzyme and enzyme stabilization system.**

(57) Stabilization systems for aqueous liquid detergent compositions containing detergent enzymes and peroxygen bleaches are disclosed. The detergent compositions contain a carboxylic acid or a mixture of carboxylic acids as an enzyme stabilizing system.

**EP 0 378 261 A3**



European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 90 20 0026

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-294904 (PROCTER & GAMBLE) * claim 1 * examples I - XII * ---	1-3, 5, 7, 8	C11D3/386
X	EP-A-86511 (PROCTER & GAMBLE) * page 12, line 31 - page 31, line 7; claims 1, 8 * ---	1, 6-8	
A	GB-A-2126242 (COLGATE-PALMOLIVE) * page 2, lines 13 - 23; claims 1-22 * ---	1, 2, 7-9	
A	EP-A-126505 (UNILEVER) * page 8, lines 23 - 32; claims 1-3 * example * -----	1-4, 6, 8	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C11D
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 12 JULY 1991	Examiner PFANNENSTEIN H.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application I : document cited for other reasons ..... & : member of the same patent family, corresponding document	

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